

THE DOUBLE VARIATION METHOD OF REFRACTIVE INDEX DETERMINATION¹

(SECOND PAPER)

R. C. EMMONS, *University of Wisconsin.*

In the preliminary paper recently published² a method was described for determining the refractive indices of crystalline substances under the petrographic microscope by using the combination of variable temperature and variable wave length of light. The advantages pointed out are much greater speed, convenience, and accuracy. The results obtained yield also a figure for the dispersion of the substance.³ I shall review briefly the essential points of the earlier paper.

SUMMARY OF PRELIMINARY PAPER.

Crystal identification by refractive index with the petrographic microscope in white light and under ordinary working conditions has well known disadvantages. Results are most commonly stated with the modification $\pm .003$ or $\pm .005$; and these results are usually secured at the cost of considerable time and painful effort. A much greater degree of accuracy is obtained by using monochromatic light as many workers have done for years. A few have sped up their determinations by employing variable temperature of the immersion medium thereby avoiding the necessity of mixing media of different index which is quite tedious. For this purpose the electrically heated stage was commonly used. It was noticed that by combining these two procedures a peculiar

¹ Several workers in this field have by personal communication from rather widely scattered points indicated their interest in the preliminary paper. I have received many friendly criticisms and suggestions which I readily acknowledge. It is intended to include in this paper replies to the points brought up in the correspondence. Dr. H. E. Merwin of the Geophysical Laboratory very kindly pointed out my incorrect use of the term dispersion as applied to the change of index with change of temperature and I have therefore altered the title from Double Dispersion to the present one.

² *American Mineralogist*, vol. 13, 1928, p. 504.

³ This was suggested as a critical determinative factor to Dr. A. N. Winchell who has concurred and has included a table of the dispersion of minerals in volume 3 of his *Optical Mineralogy*, now in the press. See also, A. N. Winchell, *American Mineralogist*, vol. 14, 1929, p. 125.

TABLE I

DISPERSION LIQUIDS	THERMAL VARIATION LIQUIDS
1. Methylene Iodide	1. Methylene Iodide
2. α -Iodonaphthalene	2. Methylene Iodide+Iodobenzene
3. α -Iodonaphthalene+ α -Bromonaphthalene	3. α -Iodonaphthalene
3a. o-Bromiodobenzene	4. α -Iodonaphthalene+ α -Bromonaphthalene
4. Phenylisothiocyanate	5. o-Bromiodobenzene
5. Iodobenzene	6. Phenylisothiocyanate
6. Bromoform	7. s-Tetrabromoethane
7. o-Toluidine	8. Iodobenzene
8. o-Nitrotoluene	9. Bromoform
9. Propylene Bromide	10. Anilin
10. Methyl Furoate	11. o-Toluidine
11. Methyl Thiocyanate	12. Nitrobenzene
12. Trimethylene Chloride	13. Ethylene Bromide
13. Ethyl Monochloroacetate	14. Propylene Bromide
	15. Pentachloroethane
	16. Methyl Furoate
	17. Methyl Thiocyanate
	18. Isoamylsulphide
	19. Ethyl Dichloroacetate
	20. Ethyl Monochloroacetate

advantage accrued, namely, that it is not often necessary to use more than one liquid to obtain a suitable dispersion curve, that is several readings at different wavelengths. If dispersion is used alone without temperature control then the reading obtained almost never falls on the soda line. Two or more readings in as many liquids are necessary in order to construct the dispersion curve from which the value for the soda line may be read. Such a procedure is laborious. Now if by varying the wavelength the index of liquid and crystal may be made to agree, then by changing the temperature five or ten degrees and thereby changing the index of the liquid, an essentially new medium is obtained. A further change in wavelength once more makes the indices coincide. In this way any number of points on the dispersion curve of the crystal may be obtained all from the same mount. If the crystal itself has high dispersion then the temperature variation alone is useful. Only a few minerals have as high a dispersion as do liquids of the same general index. The entire procedure is based on the fact that almost all liquids have a higher dispersion than crys-

tals and that the temperature coefficient of refraction of liquids is considerable whereas that of most solids is negligible. In order to enhance the value of the method an elaborate search was conducted for suitable liquids—that is liquids having both high dispersion and high temperature coefficients of refraction. These are listed in Table I which includes also a list for use of temperature variation only.

The work is best done in a dark room where there is no light from extraneous sources; also the sensitivity of the eye is slightly greater in a dark room. The apparatus needed in addition to the microscope includes a monochromator, a refractometer, an arc light, a water circulation system with thermometers and a source supply of hot and cold water. The mount is made on a cell through which the water flows. The same water passes through the refractometer on which the same immersion liquid is placed. Light from the monochromator is used to illuminate both the microscope and the refractometer. The temperature is controlled by varying the mixture of hot and cold water—both the microscope cell and the refractometer change temperature together. The wavelength of light is changed by adjusting a simple screw on the monochromator. When the proper conditions are obtained on the microscope then the light is quickly transferred to the refractometer by a mirror rotation and the index is read and corrected by the correction curve supplied with the instrument.

An essential feature of the preliminary paper is the set of liquids described in it. At that time the exact critical data of all the liquids were not known, but measurements were made on the purest liquids on hand. Further work has included careful distillation of fresh supplies and optical data are given for these definite fractions. Most of the liquids were obtained from the Eastman Kodak Co. and these were redistilled. No difficulty has been encountered thus far in duplicating with quite satisfactory accuracy any of the liquids listed. A difference of as much even as one or two in the third place of decimals in the refractive index is not serious provided the liquid used is a real narrow fraction. But closer limits than this are not difficult to obtain. If the dispersion and thermal coefficient of refraction of two supplies of liquid are not the same it does not prejudice the results provided a refractometer is used

TABLE II.

No.	Liquid	Boiling Point °C	mm.	Temperature	$N_F - N_C$		N_D		N_C		N_F						
					at 25°C	Coef.	10°C	25°C	10°C	50°C	10°C	25°C	10°C	25°C	50°C		
1.	Methylene Iodide	80	15		.00068	.0369	(1)	1.7474	1.7205	(2)	1.7375	1.7273	(3)	1.7744	1.7642	(± .0005)	1.7474
2.	α-Todonaaphthalene	160	14		.000470	.0373	(4)	1.7060	1.6989	(6)	1.6962	1.6893	(6)	1.7340	1.7266	(± .0005)	1.7142
3.	α-Iodonaaphthalene	—	—		.000468	.0338	(7)	1.6815	1.6747	(7)	1.6720	1.6653	(7)	1.7056	1.6991	(7)	1.6865
4.	Bromonaaphthalene	76	4.2		.000562	.0353		1.6555	1.6471		1.6458	1.6374		1.6817	1.6727		1.6585
5.	Phenylisothiocyanate	69-71	16.5		.000570	.0247		1.6252	1.6163		1.6179	1.6092		1.6436	1.6339		1.6196
6.	Iodobenzene	147.5	736.		.000597	.0181		1.6029	1.5935		1.5970	1.5882		1.6159	1.6063		1.5915
7.	Bromoform	87-88.5	17		.000507	.0225		1.5768	1.5690		1.5700	1.5630		1.5934	1.5855		1.5724
8.	α-Toluidine	220	740		.000492	.0228		1.5510	1.5435		1.5440	1.5372		1.5682	1.5600		1.5475
9.	Propylene Bromide	31.5-32	11.5		.000540	.0126		1.5240	1.5160		1.5198	1.5120		1.5330	1.5246		1.5113
10.	Methyl Furoate	66-66.5	9		.000451	.0166		1.4914	1.4850		1.4859	1.4799		1.5035	1.4965		1.4848
11.	Methyl Thiocyanate	33.5-34	17		.000538	.0111		1.4735	1.4659		1.4693	1.4624		1.4814	1.4735		1.4591
12.	Trimethylene Chloride	119.5	735		.000490	.0082		1.4534	1.4459		1.4504	1.4424		1.4586	1.4506		1.4387
13.	Ethyl Monochloroacetate	141.5	744		.000474	.0078		1.4265	1.4190		1.4229	1.4168		1.4309	1.4243		1.4116
3a.	o-Bromiodobenzene	305	740		.000517	.0261		1.6677	1.6600		1.6600	1.6524		1.6867	1.6785		1.6653
7.	s-Tetrahydroethane	139-42	32		.000528	.0177		1.6421	1.6340		1.6210						
10.	Anilin	67	4.5		.000523	.0245		1.5911	1.5830		1.5698						
12.	Nitrobenzene	66.8-68.5	5		.000480	.0245		1.5567	1.5490		1.5375						
13.	Ethylene Bromide	130	733		.000556	.0188		1.5435	1.5350		1.5213						
15.	Pentachloroethane	158-60	740		.000486	.0098		1.5081	1.5009		1.4886						
18.	Isoamylsulphide	80-83	10		.000449	.0091		1.4576	1.4510		1.4396						
19.	Ethyl dichloroacetate	84.5	59		.000471	.0084		1.4409	1.4339		1.4220						

(1) Calculated from Pulfrich reading at 17°C and the helium wavelength.
 (2) Calculated from Pulfrich reading at 17°C and the red hydrogen line.
 (3) Calculated from Pulfrich reading at 25°C and the blue hydrogen line.
 (4) Calculated from Pulfrich reading at 9°C and the yellow helium wavelength.
 (5) Calculated from Pulfrich reading for the yellow helium wavelength.
 (6) Calculated from Pulfrich reading for 9°C.
 (7) Calculated from Abbé reading for 15°C.
 All other readings than those for liquids one and two were made on a Bausch & Lomb direct reading refractometer at controlled temperature and wavelength of light. The light source was a Bausch & Lomb direct reading monochromator. The maximum error of these index figures is believed to be ± .0002.

in the system and the same liquid is mounted on the refractometer and on the microscope cell. For the set of liquids using temperature change alone without a refractometer the thermal coefficient of the liquids must be known. The data offered in Table I are those of entirely new distillates from those published in the preliminary paper. One change has been made—liquid no. 3 has been found objectionable in that crystals of dibromonaphthalene separate out in time. A mixture of α -Bromonaphthalene + α -Iodonaphthalene is now used. No suitable substitute has yet been found for bromoform; it therefore is still included.

Critical data for the liquids used are given in Table II. The curves for these data are shown in Figures 1 and 2.

The value of accurate temperature control has been stressed especially. Under ideal conditions the temperature of the mount and of the liquid on the refractometer will be exactly the same. Although this is impossible yet it has been found possible to make them quite reasonably close. The greatest difference between the thermometers which precede and follow the instruments is found at the highest temperatures. For the ordinary run of work one degree difference in temperature is usual, but by increasing the flow slightly this can be cut down to one-half a degree difference. For the liquids used the difference in index for each degree Centigrade ranges from .00045 to .00070. The error due to this cause is practically negligible for the ordinary run of determinative work and for careful work can be cut down to a maximum of .0003 under the most unfavorable circumstances. At lower temperatures at which the operator usually prefers to work this error is less. I would caution the operator to check the thermometers against each other for unless the two have been carefully selected they will not agree. Usually when it is necessary to resort to high temperatures (50°–60°C) it is also possible to check the result on the next liquid at a low temperature. The two results should be close and a very close figure can be estimated between them.

Dr. H. E. Merwin raised the very pertinent question⁴—“How closely does the temperature of the liquid on the microscope cell agree with the indicated temperature of the thermometers?” At his suggestion I employed the method of Ashton and Taylor⁵ to check the temperatures. The “cold junction” of a thermocouple was placed on the refractometer and the “hot” junction was placed

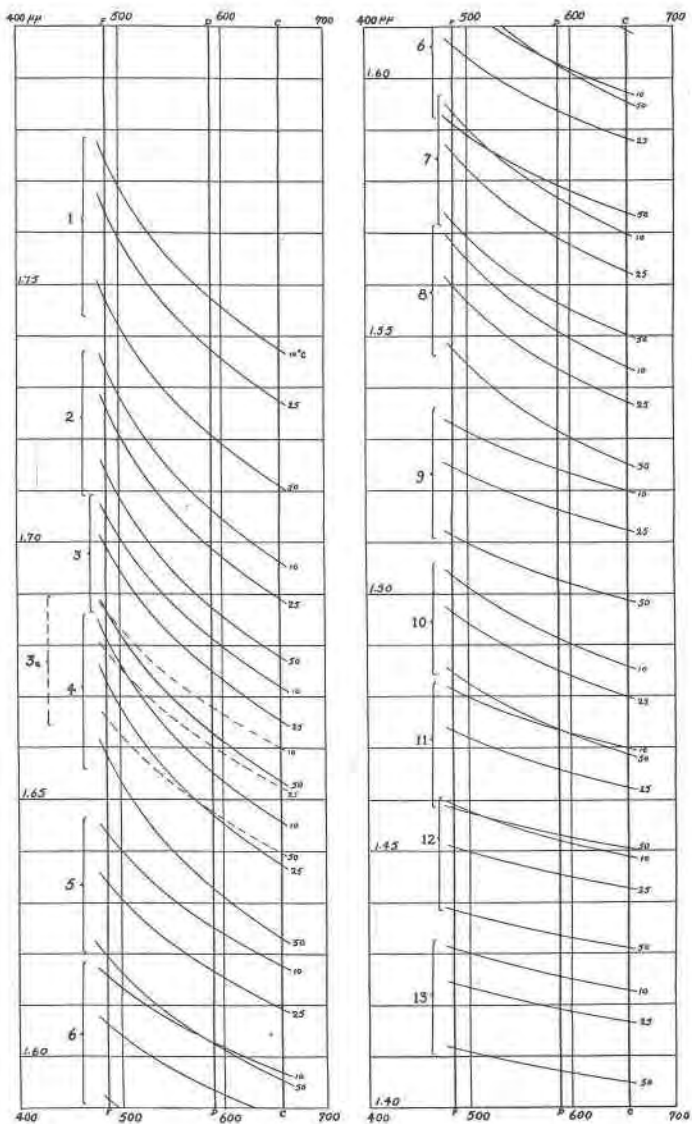


FIG. 1. Graphical representation of the dispersion and temperature coefficients of refraction of the set of liquids in which both these properties are used. This graph is intended to be used as a guide in selecting the proper liquid to be used in a determinative procedure.

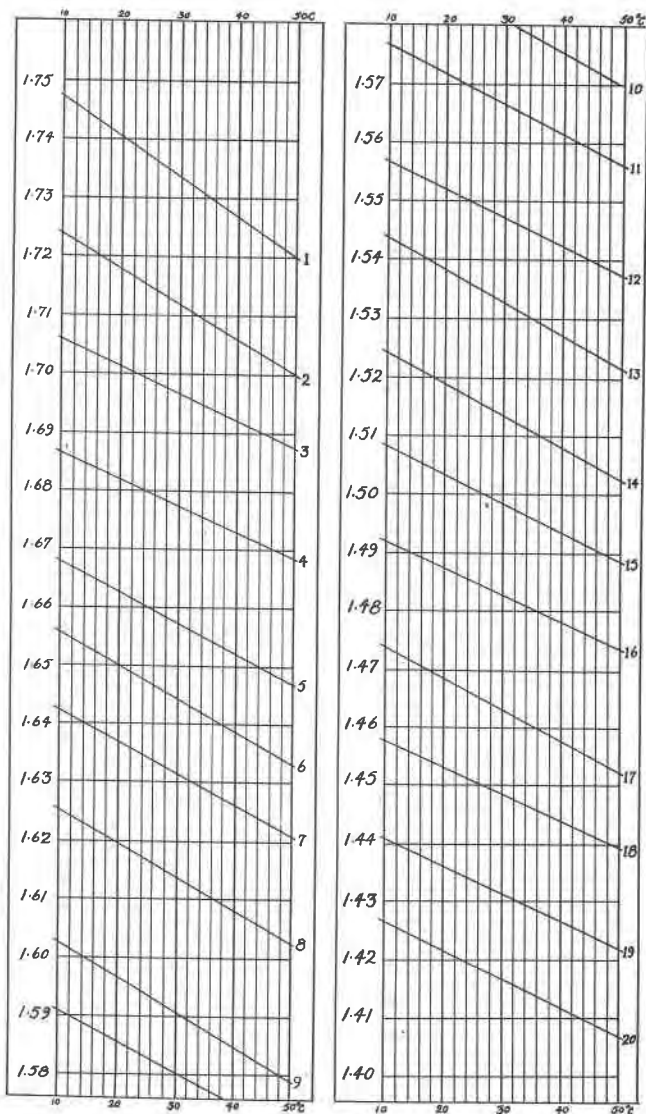


FIG. 2. Graphical representation of the index range of a set of liquids for temperature variation only. This set is intended to obviate the necessity of mixing liquids and to reduce the number of mounts necessary in a procedure, at the same time avoiding the expense of a refractometer and a monochromator.

on the water cell. A Hoskins pyrometer type "H. A." was used in which one half millivolt was subdivided and the instrument calibrated to read accurately to one half degree Centigrade and by interpolation to one quarter degree. In this way the temperature difference between the liquid on the refractometer and that on the water cell was read:

Room	temperature 27°C	
At 28.5°C	after	2 minutes difference = 0°
38.5°C	1	1°
	6	$\frac{1}{4}$ °
49.5°C	2	$1\frac{1}{4}$ °
	4	1°
	6	1°

Empirical tests indicate that these differences are quite general, and allowance can be made for them for accurate work.

A change in temperature of fifty degrees will affect the index of the glass in the refractometer. The relative importance of this source of error is indicated in the following extract from a letter from the Bausch & Lomb Optical Co.

"The temperature coefficient of glass of the type used is given as 0.0000066 t. This would mean a total index change between 10° and 50° of 0.00026. Since the scale is computed for N_d of approximately 25° this error would be slightly reduced, in that it would become plus and minus. Such a variation in index of the prism would mean about the same index change in the sample. I should say that it would never be over 0.0002 and seldom as high as that. You will understand that in this statement I am assuming a glass type, rather than the particular glass in the instrument. The temperature constants of the particular glass have never been determined."

The maximum error then on a single reading should be $\pm .0005$. Experience indicates that it is usually less. A desired reading at a particular wavelength, usually near $589\mu\mu$, is best made by taking an average.

I recently received for examination from Bausch & Lomb Optical Co. a first trial model of the set-up as they propose to make it. The accompanying photographs (Figs. 3a and 3b) show

⁴ Personal communication.

⁵ F. W. Ashton and W. C. Taylor, A Precision Method for Measuring Temperature of Refractive Index Liquids. *Am. Mineralogist*, vol. p.13, 44.

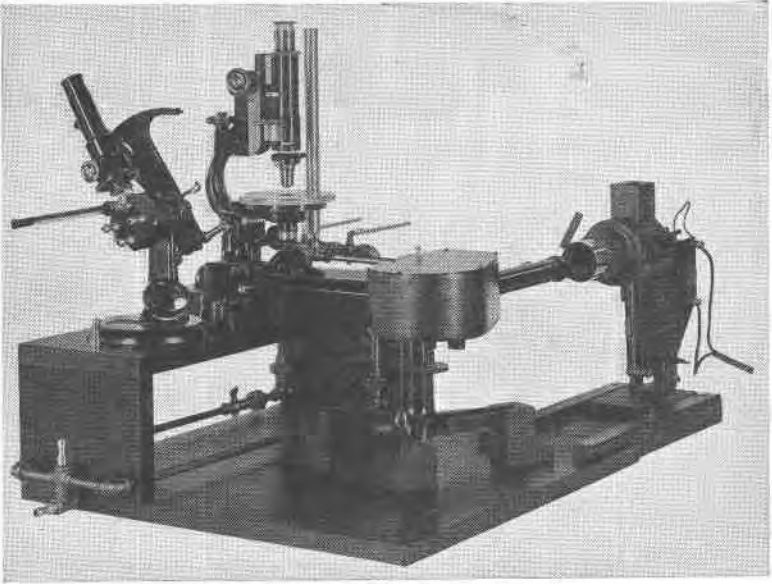


FIG. 3a. Bausch and Lomb apparatus complete but without the most recent changes.

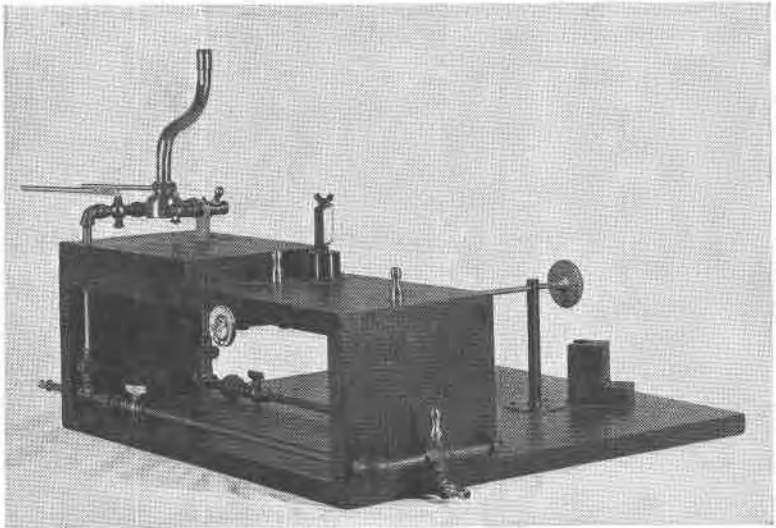


FIG. 3b. Base of Bausch and Lomb apparatus with the final improvements added.

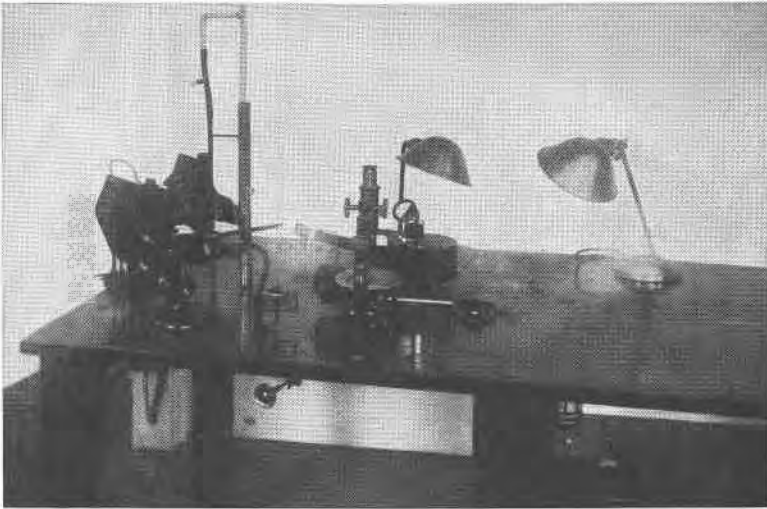


FIG. 4. Double variation apparatus being used in the Geological Laboratories at Madison.

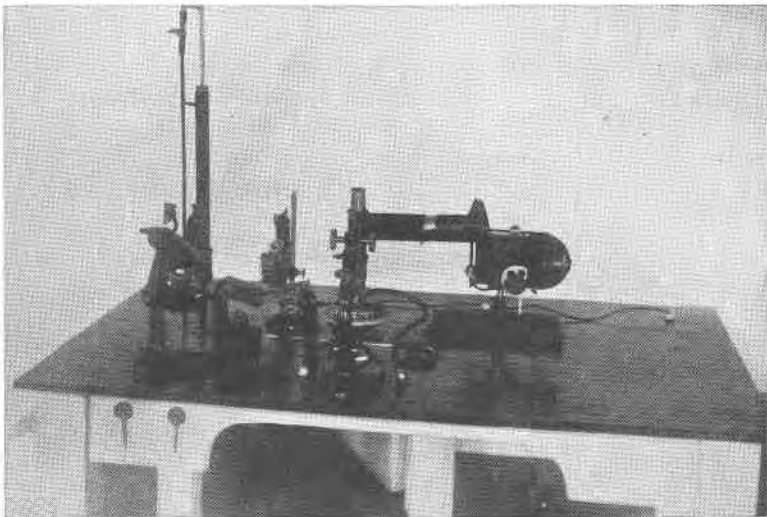


FIG. 5. Double variation apparatus being used in the Geological Laboratories at Madison.

the set-up including a few simple suggested changes recommended after the apparatus was carefully tried out in our laboratory. Bausch & Lomb instruments are used throughout.

Our own equipment was remodeled to include all modifications deemed advisable on the basis of our own experience and our observations of the Bausch & Lomb arrangement. Bausch & Lomb made some very real improvements over our original model after which theirs was designed. Two complete units are shown in Figures 4 and 5. The apparatus of Figure 4 is Bausch and Lomb equipment. For this purpose it is well to use an enclosed arc made by both companies, in which the air circulation is staggered to prevent the diffusion of light in the room. The apparatus of Figure 5 is Leitz except for the refractometer which is a Spencer model. Both Bausch & Lomb and Spencer refractometers are found quite satisfactory. The difference in mechanical manipulation is great enough to justify individual personal preference on the basis of these features. Correction curves for use with monochromatic light are supplied by both companies.⁶

The Leitz monochromator has been used with satisfaction, but I feel that the following features of the Bausch & Lomb monochromator make it more desirable for this purpose. The Bausch & Lomb instrument is direct reading in $\mu\mu$ on a four inch drum. The Leitz instrument is much more compact but is not direct reading. The scale on it is divided into one hundred units—(the F line on the instrument in Figure 5 reads 51.5 and the C line 24.2) on a 1 1/4 inch drum; readings are therefore much more accurate on the Bausch & Lomb instrument. The Bausch & Lomb instrument also has a small prism in the collimator tube for securing a comparative spectrum. The outstanding disadvantage of the Bausch & Lomb monochromator, as I see it, is its lack of dirigibility. The Leitz instrument is mounted on a very conveniently adjustable hinge which gives it a general utility not possessed by the other. The Leitz monochromator also has a neatly adjustable collimator prism which greatly facilitates illumination of the instrument. These features are pointed out in the hope of assisting those interested who are not familiar with

⁶ There are other makes of Abbé refractometer which doubtless will serve quite well; a Pulfrich is not desirable for this type of work.

both instruments, to make a selection. The importance of the monochromator for the purpose of this paper cannot be over emphasized. The monochromator should be carefully checked before being used, either with spectrum tubes or standard flames. If the Bausch & Lomb base is used then only Bausch & Lomb instruments can be made to fit without modifying the base. I feel, however, that the complete Bausch & Lomb unit is very satisfactory.

I have been asked if interference figures can be obtained with the cell in place. They cannot by any method known to me. Optic axis grains are not difficult to recognize and optic normal grains though not so easy to recognize are less often needed. To measure n_p and n_g I believe the standard method is best—namely to choose the grains of highest interference colors in the 45° position and measure a few of them, selecting extreme values. It is to overcome this recognized limitation that I have spent considerable time attempting to adapt the universal stage to this purpose. If successful it should offer an extremely rapid, accurate and generally satisfactory procedure.

In our original apparatus tap water was used directly from the mains. This has been abandoned entirely because of the dissolved air that is released from the hot water immediately on its passing the valve. Water from the mains is now run into two tanks—one hot, one cold—and from these the water for the apparatus is drawn. An overflow from the tanks keeps them at a temperature equivalent to the source temperature. The dissolved air is mostly removed while in the tanks. A bubble trap in the system removes almost all the remaining bubbles. The cell developed at considerable pains by Mr. J. S. Hipple serves very well indeed to allow the remaining bubbles to pass directly through.

On first turning on the water the flow is usually hampered by bubbles trapped in the refractometer and probably elsewhere. A few sharp taps on the tubing serve to release these and the flow increases greatly. A good flow of water is absolutely essential to good work.

Experience indicates that one of the most common sources of error on the part of students lies in failure to give the refractometer sufficient time to come to temperature. It is best to make a series of readings until two agree. If the mineral substance is

clear and gives a sharp Becke line then the reading on the microscope, after changing the temperature, can usually be made more rapidly than the refractometer can come to temperature. Students who spend more than two or three hours at a time making readings seldom secure reliable results near the end of the period. Their readings sometimes are more than .002 off, due apparently to eye fatigue.